

Article

UV Induced Photocatalytic Degradation of Caffeine Using TiO₂-H-Beta Zeolite Composite

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Abstract: An anatase phase of the TiO₂-H-beta (THB) zeolite composite photocatalyst is used for the photocatalytic degradation of caffeine, a persistent organic pollutant (POP). It is synthesized by a simple two-step sol-gel method. Phase formation, morphology, bandgap, and photocatalytic properties were analyzed using powder X-ray diffraction, scanning electron microscopy, and UV-Vis diffuse reflectance spectroscopy, respectively. The THB and the anatase TiO₂ samples were then tested for the photocatalytic activity of the degradation of caffeine. Photocatalytic studies reveal that the as-prepared THB composite showed excellent activity for the degradation of 10 ppm caffeine solution. The chemical oxygen demand (COD) analysis found caffeine to have degraded with an efficiency of 96%. Scavenging experiments indicated that the hydroxide radical played an important role in the degradation of caffeine. The results highlight the role of the H-beta zeolite as an effective support to TiO₂ and improved the photocatalytic activity. The study demonstrates that the THB composite could be effectively applied for the photocatalytic degradation of other POPs largely present in active pharmaceutical ingredients.

Keywords: photocatalysis; H-beta-TiO₂ composite; zeolite-TiO₂; anatase; caffeine



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1. Introduction

Photocatalysis offers a green solution to many of our environmental problems such as water purification, hydrogen production, organic transformation, and the decomposition of harmful organic dyes [1–4]. TiO₂, in anatase, rutile, or a mixture of anatase and rutile (Degussa), is a commonly used photocatalyst due to its impressive properties, including high thermal and chemical stability, low cost and toxicity, and wide availability [5–7]. However, there are a few shortcomings of TiO₂, such as a rapid recombination rate of electron-hole pairs, and the relatively low adsorption of organic pollutants on the surface [7–9]. Thus, to overcome these limitations, a large number of new semiconductor photocatalysts have been explored as promising alternatives [8–11]. In order to improve the photocatalytic activity of TiO₂, much work has been carried out to tune its band gap by chemical modification such as substitution or doping of chemical species [12–14]. Besides tuning the band gap, another key parameter to improve photocatalytic activity is to increase the surface area of the catalyst for the adsorption of reactants, by immobilizing it on a solid support [15–18]. In this context, zeolites are especially popular due to their excellent support properties, including high specific surface area and the ability to extensively adsorb organic pollutants. The thermal properties of the zeolites have been well documented, while currently research on their photocatalytic activity is under way [19–21]. They help excited electrons to be delocalized in the system, thus prolonging their lifetime and ultimately facilitating better UV absorption. Several reports show the enhanced degradation of common organic dyes such as rhodamine B, methylene blue, and methyl orange when exposed to efficient TiO₂-zeolite composites [22–26]. In this context, the degradation of persistent organic pollutants such as caffeine, polychlorinated biphenyl (PCBs), polychlorinated dibenzodioxins (PCDDs), and

sulfadiazine is necessary as they have a prolonged lifetime and their accumulation causes many hazards to health and the environment [27,28]. In the past decade, TiO_2 -zeolite composites have also been used to degrade many persistent organic pollutants (POP) such as caffeine and sulfadiazine [29,30]. Among the zeolites, ZSM-5, Beta, and H-beta are a few that have been commonly used as solid support due to their high surface area, which facilitates better dispersion of the TiO_2 on it [12,31,32]. Zeolite beta is a large pore crystalline aluminosilicate with a high Si /Al ratio and high surface acidity. Due to its hydrothermal stability, it serves well as a support material for various other catalysts. Mahalakshmi et al. showed the photocatalytic degradation of pesticides using the ZnO-H-beta composite [33]. Jalloul et al. reported the degradation of active pharmaceutical ingredients (API) such as tetracycline using beta zeolite composite photocatalysts [34].

The degradation of caffeine using well-known semiconductors such as zinc oxide and Degussa TiO_2 in the presence of UV and sunlight, has been reported [35–38]. Further, Ghosh et al. have reported the degradation of caffeine in solar light using a TiO_2 -ZnO composite [39,40]. Similarly, other composites of metal oxides have been used to degrade caffeine by forming a heterojunction [12]. A study of caffeine degradation using the ZnO-Zeolite A composite reported 85% degradation of 1 ppm caffeine with a catalyst amount of 700 mg [29]. However, in comparison to the current work, the amount of photocatalyst used all in the above reports is quite high, and the degradation of caffeine is not complete [31]. Therefore, in this manuscript, the addition of a small amount of H beta zeolite to the synthesized TiO_2 shows a significant increase in the degradation efficiency of the catalyst. Moreover, the amount of catalyst used is less than in prior reports. To the best of our knowledge, there are no reports on the photocatalytic degradation of caffeine using H-beta- TiO_2 composites.

In this study, the synthesized zeolite H-beta- TiO_2 composite (THB) photocatalyst is used to mineralize the POP caffeine successfully. The photocatalytic degradation of caffeine by the THB composite is followed by UV measurements. The recyclability of the catalyst and the comparison of THB with commercial anatase TiO_2 photocatalyst is discussed. The quantitative estimation of the degradation is carried out by COD analysis. This study indicates that the THB composites are promising photocatalysts for the degradation of POPs such as caffeine under UV light.

2. Experimental

2.1. Materials and Methods

2.1.1. Materials

Titanium isopropoxide (SRL Chemicals), ethanol (99% pure), potassium chromate, mercuric sulphate, silver sulphate, mercuric sulphate, ferrous ammonium sulphate, concentrated sulphuric acid, dilute sulphuric acid, and caffeine (98% pure) from Loba chemicals. Zeolite-H-beta (SAR-25) from Nankai University Catalyst Co., Tianjin, China was used.

2.1.2. Synthesis

A simple two step sol-gel method [23] is used to synthesize the TiO_2 -H-beta (5 w/v%) composite, henceforth be referred to as THB. To 2.5 mL of titanium isopropoxide, 3 mL of ethanol was added with stirring. To the mixture, 6 mL of dilute H_2SO_4 was added dropwise till a curdy white precipitate was obtained. This was then stirred until a transparent solution was obtained. The transparent solution was further stirred for 30 min to obtain a homogeneous solution. This was labelled as solution A. H-beta (0.5 g) was dissolved in 10 mL of distilled water (5 w/v%), and the solution was allowed to set at 37 °C. Then, solution A was added dropwise to this from a separating funnel and stirred for 4 h. This mixture was cooled to room temperature, aged for 13–16 h, filtered, and dried at 65–70 °C. The filtrate was calcined at 400 °C for 2 h.

2.2. Characterization of THB

Powder XRD measurements were carried out on a Rigaku Smart Lab X-ray diffractometer for TiO₂, H-beta, and THB using Cu-K_α radiation with a wavelength of 1.5418 Å. Scanning electron microscopy (SEM) images were recorded for THB and H-beta samples by a Carl Zeiss ULTRA 55 field emission instruments. SHIMADZU 2600I UV-Visible spectrophotometer was used to determine the optical band gap of the catalysts through diffuse reflectance spectra (DRS), where background correction was done by BaSO₄ (98%). Sample reflectance was recorded for the range of 200–800 nm. Additionally, the UV spectrum of the degraded and undegraded samples was also measured using the SHIMADZU 2600I spectrophotometer.

2.3. Photocatalytic Reactor

The Heber micro photoreactor used for this experiment consisted of quartz tube, transparent to UV, to which the caffeine solution and the catalyst was added. Air was circulated into the quartz tube using an air pump, to ensure the mixing of the catalyst with the solution to obtain a homogeneous reaction mixture. Two high-pressure mercury vapor lamps of wavelength 254 nm were placed behind the quartz tube. A cooling fan ensured that the reactor did not become heated due to the UV light. In the reactor, 20 mL of the solution was taken, and air was circulated through the air pump for the homogenous mixing of the catalyst in the solution.

2.4. Photocatalytic Degradation Experiment

A stock solution of 250 ppm caffeine was prepared by taking 62.5 mg of caffeine and making it up in a 250 mL standard flask with double-distilled water. Dilutions of 10 ppm were prepared from the stock. Next, 20 mL of the solution was poured into the two quartz tubes, respectively. An optimum amount of THB was added to the quartz tube, and the air pump of the reactor was switched on. Five minutes of mixing (solution and catalyst) time was allowed before switching on the UV light. After every 40 min, aliquots were collected and then centrifuged to remove any catalyst particles present in the solution for analysis using a UV-visible spectrophotometer. The experiment was performed for a duration of 160 min per trial.

2.5. Chemical Oxygen Demand (COD)

In total, 10 mL of 0.25 N potassium dichromate, 5 mL of concentrated sulphuric acid, and 5 mL of caffeine POP sample, to be analyzed, were added to a round bottom flask. To this, a pinch of silver sulphate and mercuric sulphate was added, and the mixture was digested at ~140–150 °C for 2 h. Then, it was titrated against 0.1 N ferrous ammonium sulphate (FAS) using 2–3 drops of ferroin as the indicator. The end point was the appearance of a brick-red color. The procedure was initially carried out for double-distilled water, which was the blank. Later, it was performed for the undegraded sample and the degraded sample.

3. Results and Discussion

3.1. Characterization of THB

3.1.1. Powder X-ray Diffraction (XRD)

The powder diffraction data indicates the formation of a TiO₂-H-beta (THB) composite (Figure 1). The PXRD pattern confirms there is no chemical change or structural modification of H-beta as the peaks of both TiO₂ and H-beta are observed (Figure 1). Further, as THB has no new peaks, it can be inferred that there is no impurity present in the composite. The broadened peaks in the THB pattern indicate that the crystallite size of synthesized TiO₂ is small.

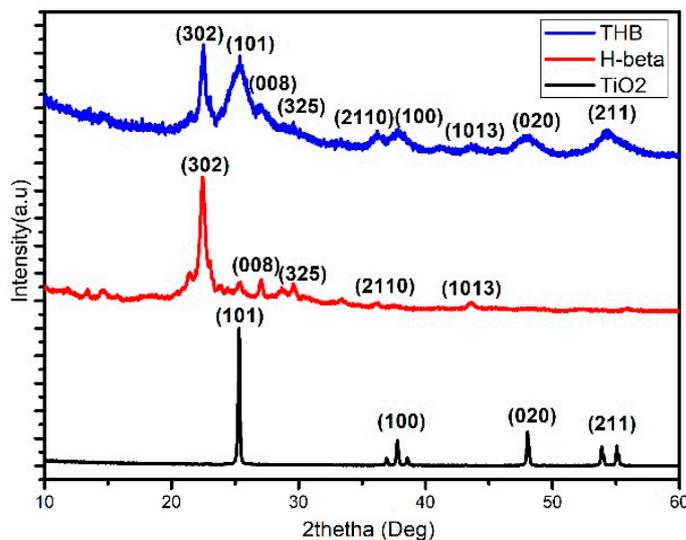
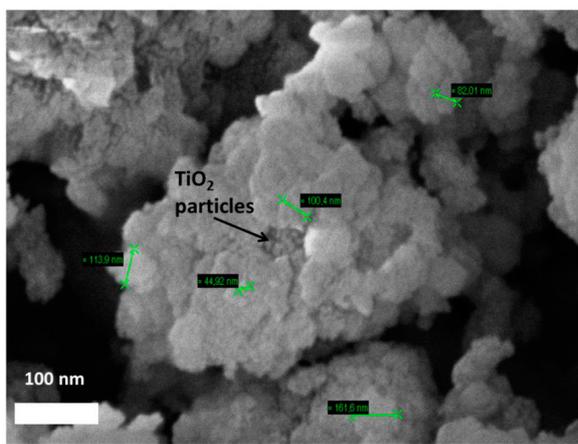


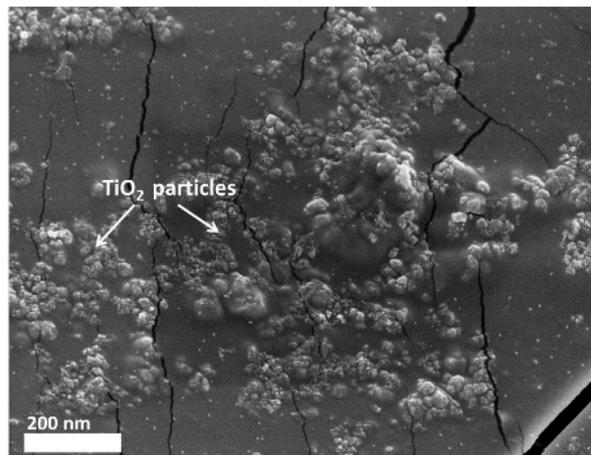
Figure 1. XRD plots of THB and comparison with commercial H-beta and standard TiO₂ (183767-ICSD) samples.

3.1.2. Morphology and Particle Size

The SEM images show agglomerated homogeneous particles for the zeolite (Figure 2a). On the other hand, the dark field image shows (Figure 2b) particles of TiO₂ dispersed on the surface of the H-beta surface. Figure 2c shows that the morphology of the zeolite, though unchanged [29,41], has TiO₂ distributed on it. The sizes of the TiO₂ particles range from 40 nm to 200 nm (Figure 2c) and confirm that THB is indeed a composite of two materials with a possibility of adsorption of TiO₂ on the zeolite surface. EDS measurements of THB show a Ti peak and a Ti-O peak, indicating the presence of TiO₂ (Figure S2).

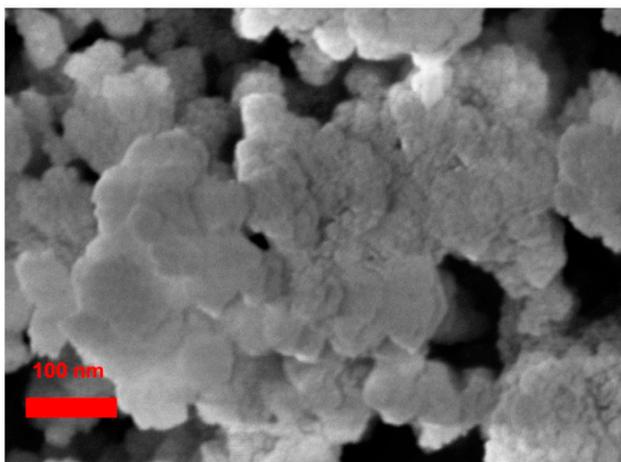


(a)



(b)

Figure 2. Cont.

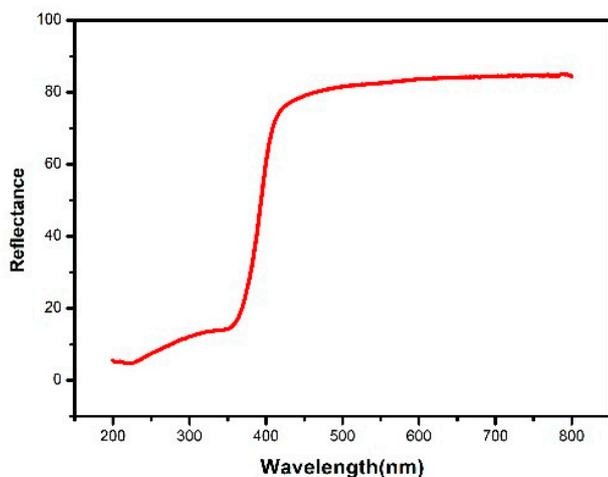


(c)

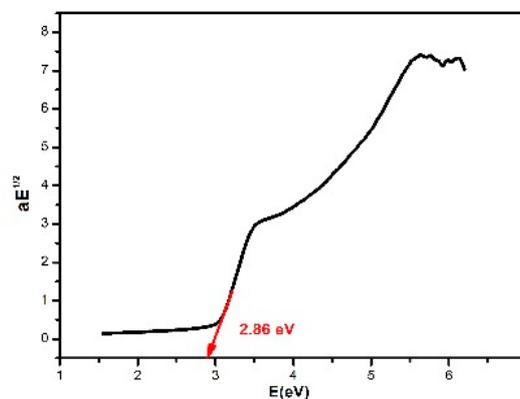
Figure 2. SEM images of (a) H-beta (b) TiO₂ particles dispersed on H-beta (c) THB composite.

3.1.3. UV-DRS (Diffuse Reflectance Spectroscopy)

The band gap of the synthesized composite THB was estimated to be 2.86 eV from the Tauc plot of the UV DRS spectrum (Figure 3a) using the Kubelka–Munk function (Figure 3b). Remarkably, the band gap of the THB catalyst is significantly less than that of anatase TiO₂ (band gap = 3.2 eV) [15].



(a)



(b)

Figure 3. (a) Reflectance vs. wavelength plot; (b) Tauc plot of THB plotted using THB Kubelka–Munk function.

3.2. Photocatalysis

The photocatalytic activity of the THB composite was evaluated for the degradation of caffeine using UV radiation. The UV visible spectrum of the caffeine molecule shows two peaks, one at 205 nm and another one at 272 nm (Figure 4).

From the structure of caffeine, we predict that the carbonyl group undergoes a $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition. Thus, the peak at 205 nm is due to $\pi \rightarrow \pi^*$ corresponding to the conjugation present in the ring and carbonyl groups, and the peak at 272 nm is due to the $n \rightarrow \pi^*$ transition corresponding to the carbonyl groups. The degradation of caffeine by photocatalysis can be monitored by following the decrease in intensity of the second peak (peak at 272 nm), considered as the characteristic peak of caffeine (Figure 4).

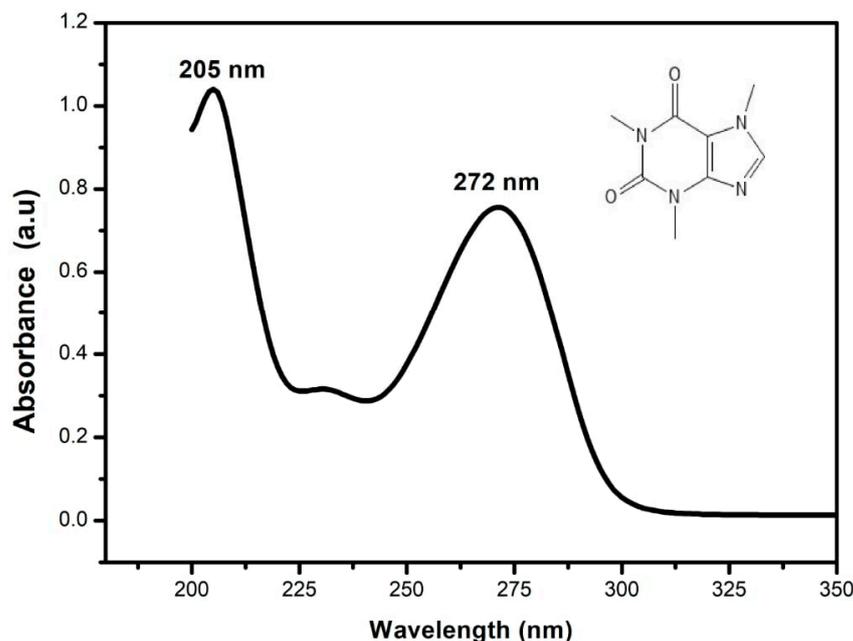


Figure 4. UV spectra of caffeine before photocatalytic degradation.

The photocatalytic degradation of caffeine was qualitatively followed by measuring the UV spectra of the original and degraded caffeine at different times. It can be clearly observed from the spectra that there is a gradual decrease in the intensity of the peak at 272 nm ($n \rightarrow \pi^*$ transition) (Figure 5), which indicates the breakage of bonds corresponding to carbonyl groups. Thus, as the photocatalysis progressed, the UV spectrum established the structural destruction of the 10 ppm caffeine molecules suspended in THB catalyst and illuminated by UV light.

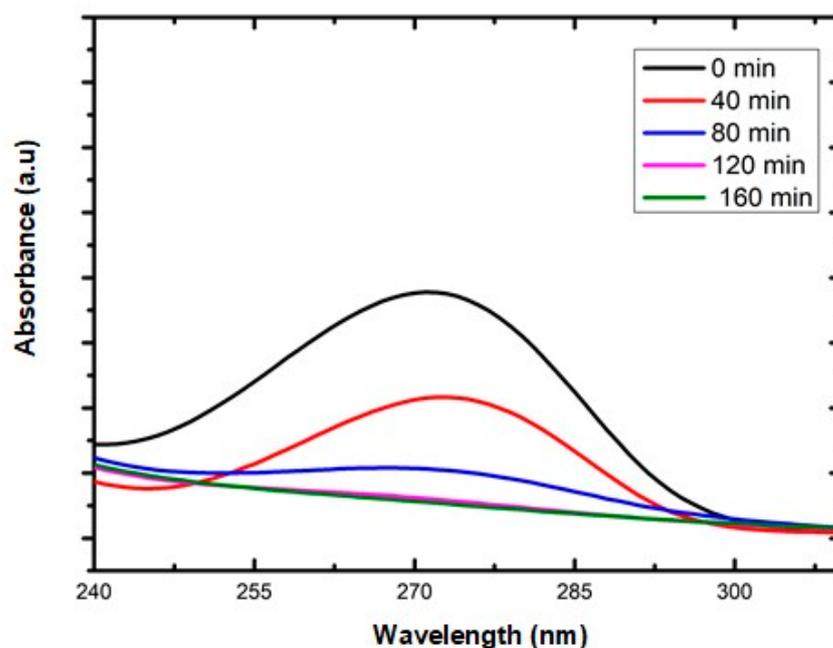


Figure 5. UV spectra of 10 ppm caffeine degradation using 35 mg catalyst.

Initially, a blank experiment was conducted, where a suspension of 10 ppm of caffeine solution and an optimum amount of the catalyst was stirred using the air pump, in the dark before irradiation. There was no degradation of caffeine solution in the absence of

light. Following this, the experiment was carried out in the presence of UV light and the THB photocatalyst. Figure 6a,b display the degradation profile and degradation efficiency of caffeine in the presence of THB under UV radiation. For comparison, the degradation of caffeine by commercially obtained anatase TiO₂ was carried out under UV irradiation in the same experimental conditions (Figure 6a,b).

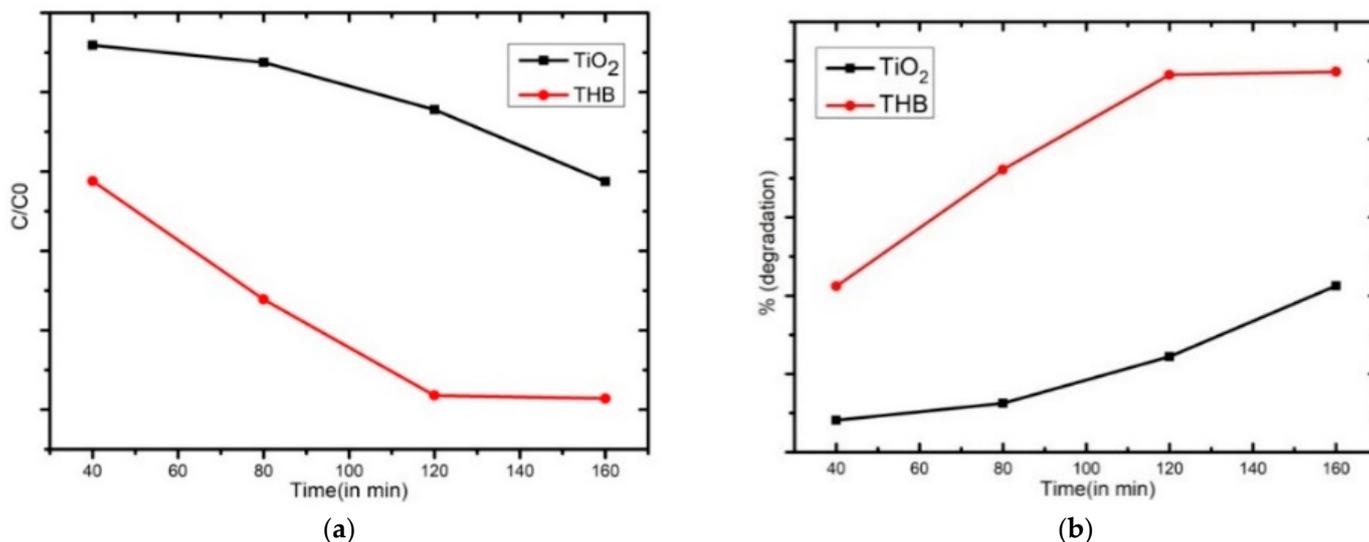


Figure 6. (a) Degradation profile for 10 ppm caffeine using TiO₂ and THB catalyst. (b) Degradation efficiency of TiO₂ vs. THB photocatalyst to degrade 10 ppm caffeine solution.

The photocatalytic degradation profiles of THB and TiO₂ (Figure 6a,b) show that THB exhibits a significantly higher photocatalytic degradation of 95% in 120 min, while TiO₂ was able to degrade less than 50% of the 10 ppm caffeine solution at the same time. The degradation efficiency of the photocatalyst can be calculated using the following equation: %degradation = $(C_0 - C/C_0) \times 100$, where C_0 is the initial concentration and C is the concentration of the dye at a given time. It is found that THB degrades 95% of 10 ppm caffeine (Figure 6), whereas anatase TiO₂ removes only 50% of the dye (Figure 6). Though anatase with a band gap of 3.2 eV is expected to degrade caffeine faster, it is remarkable that the rate of degradation is higher for the THB composite catalyst. Thus, it can be stated that the THB photocatalyst is more efficient than anatase TiO₂ for the photocatalytic degradation of caffeine. This could indicate that the H-Beta zeolite helps in the efficient distribution of TiO₂ on its surface, thus resulting in more active sites of TiO₂ in contact with the caffeine solution for enhanced degradation.

3.2.1. Effect of Catalyst Amount and Caffeine Concentration on the Degradation

Further, to find the optimum amount of catalyst that enables maximum degradation of caffeine solution in minimum time, three separate trials were carried out with 15 mg, 25 mg, and 35 mg of catalyst for 5 ppm, 10 ppm, and 15 ppm of caffeine solution, respectively. For the first set of experiments, the catalyst amount was varied, and the caffeine concentration was kept constant. Then, the caffeine concentration was varied, keeping the catalyst amount constant.

The degradation profile and efficiency for the various trials are shown in the ESI (Figures S3 and S4). From these trials, it can be observed that more than 95% degradation is observed for the 35 mg of catalyst for an optimum concentration of 10 ppm (Figure 7a,b). Thus, it can be inferred that 35 mg of THB is the optimum concentration of the catalyst for the degradation of 10 ppm caffeine solution.

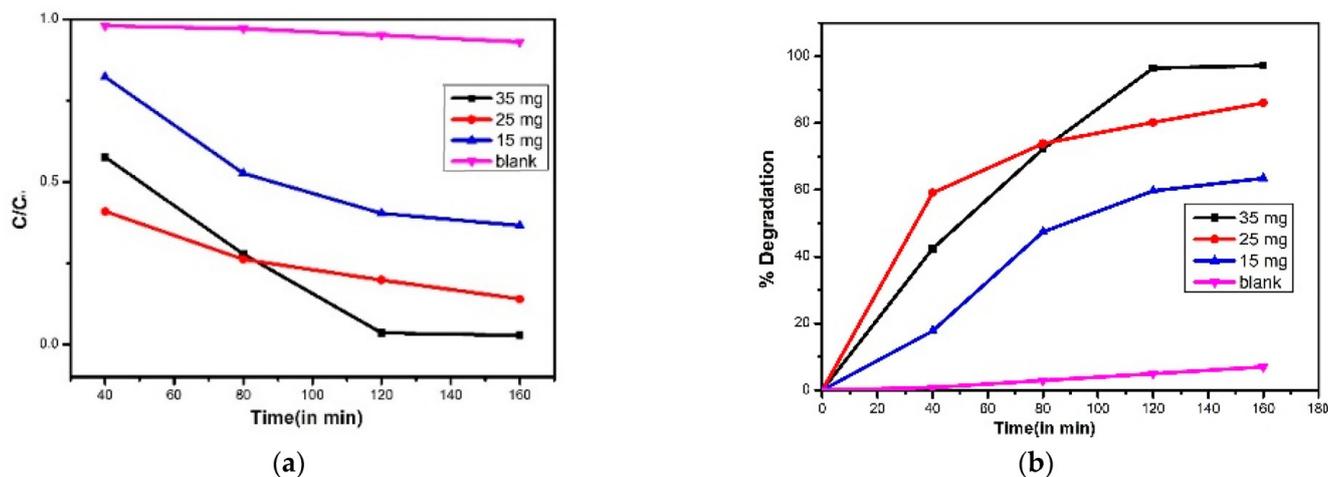


Figure 7. (a) Degradation profile for 10 ppm caffeine using 15 mg, 35 mg, and 25 mg catalyst. (b) Degradation efficiency of 15 mg, 25 mg, and 35 mg of catalyst for degrading 10 ppm caffeine solution.

3.2.2. Reusability of Catalyst

To test the reusability of the catalyst, the experiment was carried out for three complete cycles. After the reaction mixture was centrifuged, the catalyst was thoroughly washed with water to remove adhered caffeine molecules and used for the next cycle of photocatalysis reaction. From Figure 8a,b, it can be seen that there is some reduction in catalytic activity in the third cycle. This could be attributed to the increased adherence of the caffeine molecules on the catalyst surface, hindering the active sites for further reaction.

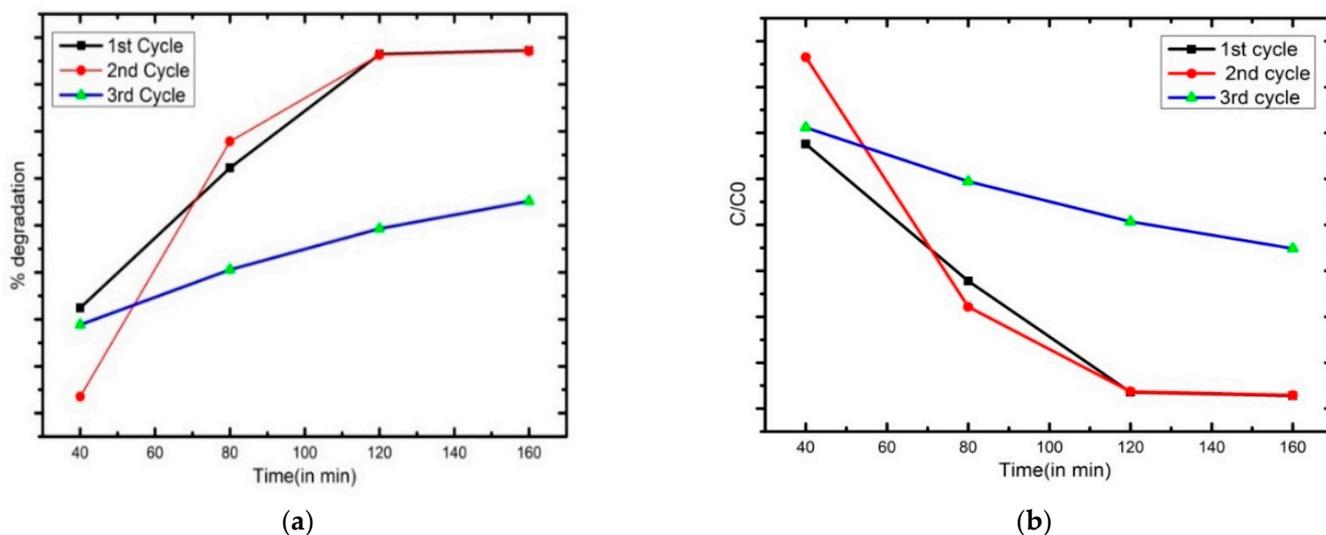


Figure 8. (a) Degradation profile for 10 ppm caffeine after reusing the THB catalyst for three cycles. (b) Degradation efficiency of 35 mg of THB for degrading 10 ppm caffeine solution for three cycles.

3.2.3. Photocatalytic Mechanism

It is well known that the photocatalytic degradation of organic pollutants is facilitated by various reactive species such as hydroxyl radical, holes, and superoxides. Therefore, scavengers such as isopropyl alcohol (IPA), KI, and $AgNO_3$ are utilized to investigate the primary radical that is responsible for the degradation (Figure 9). The IPA scavenges the photogenerated hydroxyl radical, while KI traps holes and $AgNO_3$ removes the reactive superoxide species. When IPA or KI was added to the caffeine solution along with the photocatalyst, no significant change in the photocatalytic degradation was observed (Figure 9). However, when $AgNO_3$ was added, the degradation of caffeine was suppressed.

Thus, it can be inferred that while holes and superoxide radicals do not play a key role, the hydroxide radicals drive the photocatalytic degradation of caffeine. Therefore, the mechanistic pathway for the degradation of caffeine can be tentatively shown from the trapping experiments (Figure 10). Once light is incident on the photocatalyst, the photogenerated holes present in the valence band oxidizes the hydroxide ions to produce hydroxide radicals, which are responsible for the degradation of caffeine. Based on these observations, a tentative mechanism for the mineralization of caffeine is proposed below.

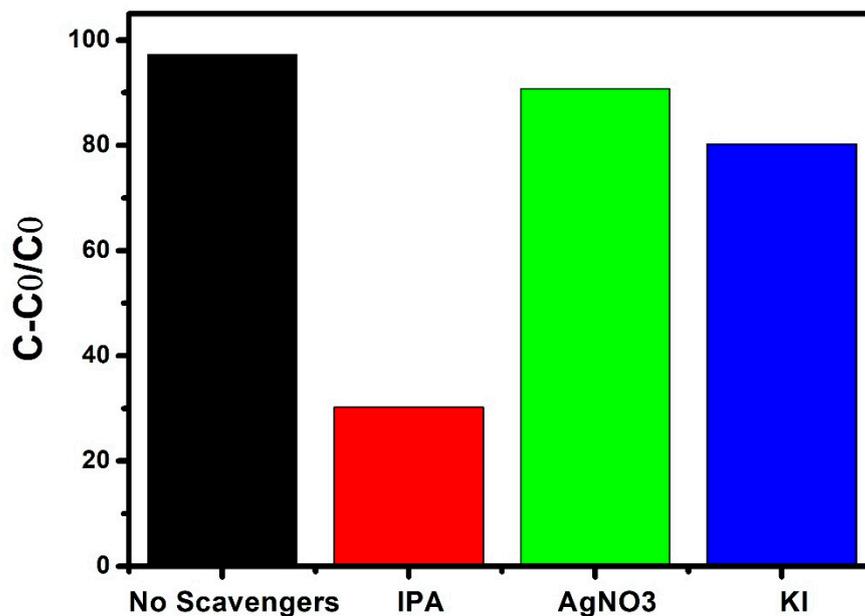


Figure 9. Photocatalytic degradation mechanism of caffeine.

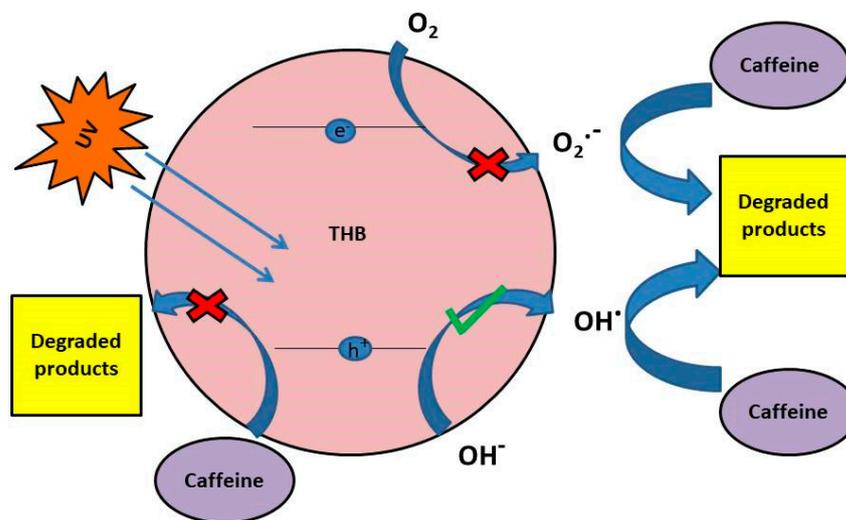
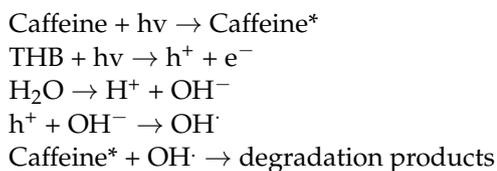


Figure 10. Schematic representation of photocatalytic degradation of caffeine.



3.3. Chemical Oxygen Demand (COD)

Further, the extent of degradation of caffeine molecules was estimated quantitatively through COD method (chemical oxygen demand). In this method, the amount of dichromate consumed in the reaction is a direct measure of O₂ required to oxidize the organic matter into CO₂ and H₂O. In this procedure, COD was carried out for 10 ppm caffeine before and after its degradation using the THB composite for 120 min. The COD values were calculated from the formula given below

$$\text{COD} = \frac{(V_b - V_s) \times \text{Normality of FAS} \times 8 \times 1000}{\text{Volume of sample}}$$

where V_b is the titer value of blank and V_s = the titer value of the sample.

The COD values for the initial caffeine sample of concentration 10 ppm caffeine solution was found to be 2480 ppm, while for the final sample (after complete degradation by THB for 120 min) it was found to be 96 ppm. This shows nearly 96% degradation, also implying that almost complete mineralization of caffeine takes place in 120 min.

There could be several explanations for the enhanced photocatalytic activity of the THB composite compared to anatase TiO₂ samples. According to the literature [34], the H-Beta zeolite itself does not participate in the degradation of caffeine; rather, it acts as a solid support for the TiO₂. This implies that the TiO₂ particles are effectively dispersed on the zeolite support. Thus, by preventing their agglomeration, the zeolite provides a much higher surface area and thereby increases the availability of active sites in TiO₂. Moreover, from the literature it can be conjectured that the high surface area of the zeolite could reduce recombination rate of the electron–hole pairs generated during the photocatalytic process [26,30,42]. Thus, in these composites, the surface area plays an important role in increasing the rate of degradation. Additionally, as inferred from the DRS, the THB composite has a reduced bandgap that could aid in the increased absorption of UV photons. All of these factors in synergy could enable this composite to exhibit better photocatalytic activity for the degradation of caffeine than anatase TiO₂.

4. Conclusions

THB composite photocatalyst was successfully synthesized by two step sol-gel process and characterized by both powder XRD and SEM-EDS. From UV-DRS, the band gap of THB is 2.86 eV, which is less than 3.2 eV of TiO₂. In total, 95% of 10 ppm caffeine solution could be degraded by UV photocatalysis using THB composite within 120 min, while only 50% could be degraded by anatase TiO₂ under similar conditions. This degradation is qualitatively followed by UV measurements of the degraded product for various intervals of time. Scavenging experiments show that the hydroxide radical plays a key role in the degradation mechanism of caffeine. COD measurements quantitatively confirmed the almost mineralization of 10 ppm caffeine molecules. The reusability of the catalyst was also tested, and THB retained its activity till the end of 2nd cycle. The improved photocatalysis is attributed to the high surface area of the zeolite and the decreased band gap of the composite. In conclusion, THB is a much better catalyst than TiO₂ for caffeine degradation and an eco-friendly and inexpensive way to overcome the problem of ever-increasing caffeine pollution. This study can further be extended to include the degradation of other discarded APIs.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min13040465/s1>, Figure S1: Schematic representation of two step sol-gel process used to prepare the THB; Figure S2. The EDAX spectral distribution of THB composite; Figure S3: (a) Photocatalytic degradation profile for 5 ppm caffeine solution (b) Degradation efficiency; Figure S4: (a) Photocatalytic degradation profile for 15 ppm caffeine solution (b) Degradation efficiency.

Author Contributions: Conceptualization, J.Q.D. and N.G.S.; Methodology, G.G.; Software, G.G.; Validation, N.G.S.; Formal analysis, G.G.; Investigation, G.G.; Data curation, G.G.; Writing—original

draft, N.G.S.; Writing—review & editing, J.Q.D.; Visualization, N.G.S.; Supervision, N.G.S. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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